

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 794 428 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.09.1997 Bulletin 1997/37

(51) Int Cl.⁶: G01N 27/12

(21) Application number: 97301435.0

(22) Date of filing: 04.03.1997

(84) Designated Contracting States:
CH DE FR GB IT LI NL SE

• Hinton, Andrew John
Hampshire GU13 0LU (GB)

(30) Priority: 04.03.1996 GB 9604627

(74) Representative:
Hedley, Nicholas James Matthew et al
Stephenson Harwood
One, St. Paul's Churchyard
London EC4M 8SH (GB)

(71) Applicant: NEOTRONICS LIMITED
Bishop's Stortford Hertfordshire CM22 6PU (GB)

(72) Inventors:
• Cooke, Michael
Bampton, Devon EX16 9NJ (GB)

(54) Sensor for volatile materials and gases

(57) A sensor capable of distinguishing between different optical isomers (enantiomers), which sensor comprises a pair of spaced-apart contacts ((14) and a semi-conductive polymer material (20) spanning the gap (15) between the contacts, which polymer material

includes chiral sites. The chiral sites in the polymer material are preferably formed by incorporating an optically active counterion into the polymer material, for example by growing the polymer in the presence of such a counterion. e.g. camphor sulphonic acid.

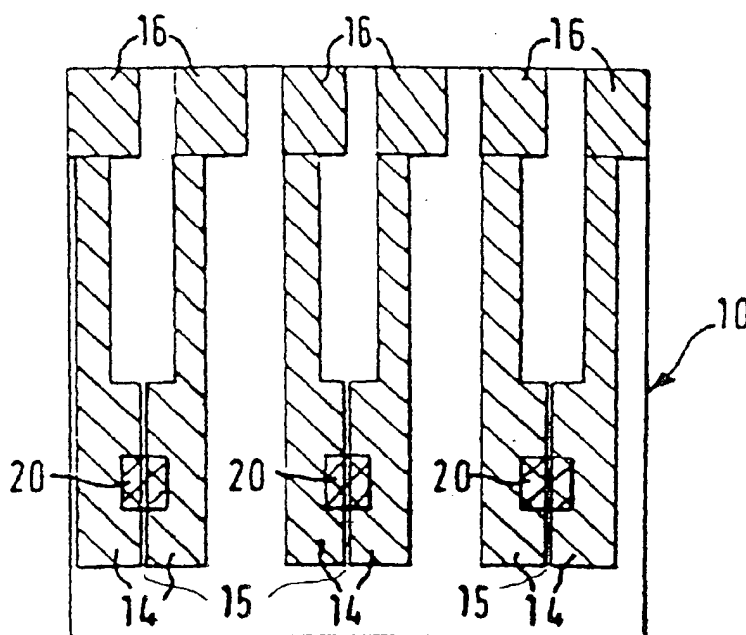


FIG. 7

EP 0 794 428 A1

Description

Technical Field

The present invention relates to the sensing of gases, volatile materials and in particular to the sensing of smells, aromas or odours.

Background Art

It is known that the smell of certain naturally occurring volatile materials, as perceived by the human nose, is dependent upon the optical activity of the volatile material. For example, d-carvone smells of caraway and dill while the corresponding l-carvone smells of spearmint. It is thus highly desirable to be able to distinguish between different optical isomers (enantiomers). However, optical isomers have identical physical properties to each other and it is therefore difficult to tell the isomers apart using simple analytical techniques without separating out the individual isomers and no such simple technique has hitherto been able to achieve this.

Although optically active aroma materials can be produced synthetically, synthetic production generally produces a racemic mixture of the isomers and the separation of the racemic mixture into its constituent isomers is very expensive. The aroma effect of the racemic mixture is often different from that of the naturally occurring isomer. On the other hand, synthetically produced racemic aroma materials are much cheaper than their naturally occurring counterparts.

It is possible, in order to save costs, to incorporate a limited amount of the synthetic material in with the naturally-occurring material without a significantly noticeable effect on the overall aroma but there is a limit to how much synthetic material can be incorporated before it does have a noticeable effect. For example, l-menthol is added to toothpaste to give it a peppermint flavour. l-menthol is naturally occurring but it can also be produced synthetically in a racemic mixture. The racemic mixture of d- and l- isomers is much cheaper than the naturally occurring l-menthol but, as stated, there is a limit on how much synthetic menthol can be added before the user notices. It is therefore highly desirable to be able to detect the difference between synthetic and naturally occurring menthol to control the amounts of the natural and synthetic menthol added to toothpaste.

The present invention provides a simple sensor that is capable of producing a signal that distinguishes between different enantiomers.

It is known from GB-2176901, GB-2221761, WO93/03355 and WO86/01599 to make sensors for sensing the presence of volatile materials, e.g. smells, aromas and odours, in a gaseous atmosphere. Such sensors consist of a pair of spaced-apart electrical contacts and a semi-conductive polymer spanning the gap between the contacts. The resistance of the polymer changes on exposure to a volatile material, the magni-

tude of the resistance change depending firstly on the nature and amount of the volatile material and secondly on the nature of the polymer.

It is also known to provide a sensing head for analysing a volatile material that comprises an array of such sensors, each containing a different polymer. The different polymers in the sensors of the head respond differently to the presence of a volatile material, e.g. an aroma, in the atmosphere being monitored. The resistance of the polymers of the various sensors sensor head are monitored to give an output signal for each sensor, which may, in effect, be a plot of the resistance of the polymer of each sensor against time. The combination of signals from the various sensors gives a pattern that is characteristic of the aroma concerned and the pattern of sensor signals for a given aroma is often referred to as a "fingerprint" of that aroma. The combination of sensor signals obtained on exposure of the sensor head to a volatile material can be used to detect, characterise and identify the smell, aroma or odour.

The sensors are made by laying down on a substrate a pair of spaced-apart contacts and the polymer is grown (polymerised) electrolytically in the gap between the contacts by dipping the spaced-apart contacts into a monomer solution that also contains a counter ion and a solvent. When an electric current is passed between, on the one hand, the contacts and, on the other hand, a counter electrode, the monomer is polymerised in the gap between the contacts. The properties of the polymer within the sensor is determined, not only by the monomer, but also by the counterion present in the monomer solution, which is incorporated into the polymer to balance the ionic charge of the polymer chain. Also the properties of the polymer are affected by the nature of the solvent in the original monomer solution.

Disclosure of the Invention

According to the present invention, there is provided a sensor capable of distinguishing between different enantiomers, which sensor comprises a pair of spaced-apart contacts and a semi-conductive polymer material spanning the gap between the contacts, which polymer material includes chiral sites.

The chiral sites in the polymer material may be formed by:

1. including optically active groups in the polymer, generally in a side group bonded to the chain; for example, when the polymer is polypyrrole, the chiral side chains may be bonded to one of the carbon atoms or to the nitrogen atom of the pyrrole ring in the oxidised polypyrrole;
2. incorporating an optically active counterion into the polymer material, for example by growing the polymer in the presence of such a counterion; examples of such counterions are menthoxy acetic acid, carzyl acetate and natural or synthetic chiral

amino acids such as cysteine and valine, or
3. growing the polymer from a monomer solution whose solvent is optically active.

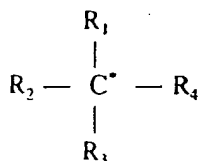
Although sensors as described in WO 93/03355 are capable of detecting aromas and the human nose is also capable of detecting aromas, the sensors themselves do not actually mimic the action of the nose since the sensors and the nose use completely different mechanisms for detecting aromas. The sensors detecting the conductivity of the polymer in the presence of the aromas while the human nose detects aromas because the aroma triggers nerve cells in the nose that the brain responds to. It is thus totally unexpected and surprising that the sensors can detect differences in enantiomers in this way, particularly since the physical properties of the enantiomers are identical to each other (apart from their effect on polarised light).

The polymer may be a copolymer.

Of the above three possibilities of including a chiral site, possibility 2 is preferred since it is easier to incorporate chiral counterions into the polymer material during the growth of the polymer chain than to incorporate such sites into the polymer itself, since steric effects can lead to problems in polymerising monomers having chiral sites. The use of optically active solvents in the monomer solution can give the desired discrimination between enantiomers, but it is less reliable than the use of optically active counterions and/or optically active sites in the polymer itself.

The optically active anionic counterion preferably includes a sulphonic acid (sulphonate) group since that stabilises the polymer material in air. The sulphonic acid group is preferably bonded directly to the optically active site although this is not an absolute necessity.

The counterion is preferably a compound of a general formula:



wherein R_1 , R_2 , R_3 and R_4 are all different and stand for different organic or inorganic substituents; preferably at least one of the substituents is or contains one or more sulphonate group(s) (although it is apparent that two or more of the substituents R_1 to R_4 cannot stand for sulphonate alone). Most preferred are commercially available optically active compounds, especially camphor sulphonic acid, which gives rise to the camphor sulphonate anion.

When the optically active site is included in the polymer chain, it is generally included in a side chain to the polymer backbone, for the reasons given above. Any

natural or synthetic optically active side group may be used so long as it can be introduced into the polymer chain. Example of such side groups are radicals formed from menthoxy acetic acid, carzyl acetate and natural or synthetic chiral amino acids such as cysteine and valine.

The chiral sites may be introduced into the polymer by an optically active solvent. In these circumstances, any suitable optically active solvent may be used.

The present invention also contemplates a method of detecting and discriminating between different chiral compounds, which comprises exposing a sensor of the type described above to a gaseous sample containing an optically active substance and measuring the resistance of the polymer material.

The present invention is not limited to the detection of aroma materials and can be used to detect gases and volatile materials that are odourless to the human nose. The gaseous sample may be the gas or vapour in the headspace above a volatile liquid or solid.

Brief Description of the Drawings

Figure 1 is a graph showing the signals (against time) from twelve sensors according to the present invention on exposure of the sensor to (S)-(+)-2-amino-1-butanol;

Figure 2 is a graph corresponding to Figure 1 when the same twelve sensors are exposed to (R)-(-)-2-amino-1-butanol;

Figure 3 is a graph showing the difference, for each sensor, between the signal of the sensor when exposed to (R)-(-)-2-amino-1-butanol as compared to the signal of the sensor when exposed to the (S) isomer, i.e. it is a plot of the difference between the graphs of Figures 1 and 2;

Figure 4 shows a plot of the difference in the signals of twelve sensors when exposed to (R)-(+)-limonene and (S)-(-)-limonene;

Figure 5 shows a polar plot of the signal from ten sensors exposed to (S)-(+)-carvone;

Figure 6 is a polar plot similar to Figure 5 but showing the response of twelve sensors of same type used in connection with the plot of figure 5 when exposed to (R)-(-)-carvone.

Figure 7 is a schematic view of three sensors of the present invention mounted on a common base.

Best Mode for Carrying out the Invention

Example 1

A substrate containing three sensors of the present invention is made in the manner disclosed in WO93/03355 (the content of which is incorporated herein by reference). The substrate (see Figure 7) includes a base 10 of silicon, alumina or silica on which there are deposited three pairs of contacts 14 (one pair for each sensor), the contacts of each pair being spaced apart by a gap 15 of approximately 10 μm . Electrical connections to the individual contacts 14 can be made by conductive pads 16. The whole of the substrate (except in the area of the pads 16 and in the area of a window 20 overlying both the gap 15 and adjacent areas of the contacts) is covered by a layer of an insulating stop-off material (not shown for ease of illustration). Details for the manufacture of the substrate are disclosed in WO93/03355.

25 ml of 0.1M (1R)(-)-10-camphor sulphonic acid solution (the solvent being deionised water) is measured into a beaker and 0.25 grams of purified pyrrole are added drop by drop using a teat pipette. The resulting pyrrole solution is stirred with a glass rod.

The substrate is immersed in the pyrrole solution so as to cover the window 20 where the polypyrrole will be grown. A saturated calomel reference electrode and a platinum gauze secondary (counter) electrode are also inserted into the solution. The contacts 14 of the substrate and the secondary and the reference electrodes are then all connected to a conventional potentiostatic circuit that maintains a potential of +850 millivolts between, on the one hand, the contacts 14 and, on the other hand, the reference electrode. This causes the pyrrole to polymerise in the window 20 of each sensor. After two minutes, the potentiostatic circuit is switched off and the polypyrrole grown on the substrate is allowed to equilibrate with the pyrrole solution for a further two minutes before being removed from the solution and rinsed with distilled water. The substrate is allowed to dry for 24 hours.

Example 2

The procedure described in Example 1 is followed except that the (1S)(+) enantiomer of camphor sulphonic acid is used instead of the (1R)(-) enantiomer.

Example 3

Six sensors of the type described in Example 1 and six sensors of the type described in Example 2 are mounted on a sensor head of a type commercially available from Neotronics Scientific Limited of Western House, 2 Cambridge Road, Stansted Mountfitchet, Essex, United Kingdom and each is connected to a circuit for measuring the resistance of the polypyrrole depos-

ited in the window 20. This involves applying a potential difference between the contacts 14 of each sensor so that an electrical current passes through the polypyrrole; the magnitude of the current flowing will give a measure of the resistance of the polymer. These sensors are then exposed to an atmosphere containing (S)-(+)-2-amino-1-butanol at a temperature of approximately 20°C and the resulting signals from the various sensors are shown in Figure 1 where the vertical axis is the sensor signal (i.e. change in resistance) and the horizontal axis denotes time in minutes. The sensors are then removed from the 2-amino-1-butanol atmosphere and allowed to equilibrate in dry air for a period of at least 5 minutes.

The sensors are then exposed to an atmosphere containing the (R)(-) enantiomer of 2-amino-1-butanol and the resulting signals from the sensors are shown in Figure 2.

It is apparent from the graph of Figures 1 and 2 that the two types of sensors are able to discriminate between the two enantiomers of 2-amino-1-butanol and also that the signals from the sensors of Example 1 give qualitatively similar signals to the two chiral gas samples as the sensors of Example 2, despite the polymers in the two sensors having opposite chiral sites.

The difference between the signal of each sensor when exposed to the (R)(-) enantiomer and the signal when exposed to the (S)(+) enantiomer is shown in Figure 3 which clearly shows that all the sensors are able to discriminate between the two enantiomers.

Example 4

A procedure similar to that described in Example 3 is repeated except that the sensors are exposed in turn to the two enantiomers of limonene. The resulting difference plot is shown in Figure 4.

It is clear from Figure 4 that the sensors are able to discriminate between the two enantiomers of limonene.

Example 5

The procedure of Example 1 was followed except that a racemic mixture of sodium camphor sulphonate was used instead of resolved (R)(-) camphor sulphonic acid.

Example 6

Ten sensors made by the procedure set out in Example 5 were exposed to the (S)(+)-carvone and the resulting steady-state signals from the sensors are shown in the polar plot of Figure 5.

Twelve sensors of the same type were then exposed to (R)(-)-carvone and the resulting polar plot (on the same scale as in Figure 5) is shown in Figure 6.

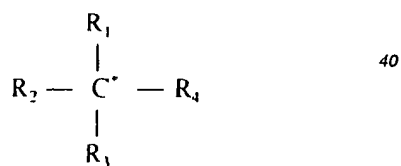
It is clear from a comparison between Figures 5 and 6 that the sensors are able to discriminate between the two enantiomers of carvone. Note should be taken that

a polymer containing a racemic mixture of the counterion was still able to discriminate between the two enantiomers of carvone indicating that it is not necessary for all the sites in the polymer to have the same chirality in order to discriminate between different enantiomers.

5

Claims

1. A sensor capable of distinguishing between different volatile enantiomeric substances in the gaseous phase, which sensor comprises a pair of spaced-apart contacts and a semi-conductive polymer material spanning the gap between the contacts, wherein the polymer material is such that its electrical resistance changes on exposure to volatile enantiomeric substances and wherein the polymer material includes chiral sites. 10 15
2. A sensor as claimed in claim 1, wherein the chiral sites in the polymer material are formed by a chiral counterion incorporated into the polymer material, for example by growing the polymer in the presence of such a counterion. 20 25
3. A sensor as claimed in claim 2, wherein the optically active anionic counterion includes a sulphonic acid (sulphonate) group.
4. A sensor as claimed in claim 3, wherein the sulphonic acid group is bonded directly to the optically active site. 30
5. A sensor as claimed in any one of claims 2 to 4, wherein the counterion is a compound of a general formula: 35

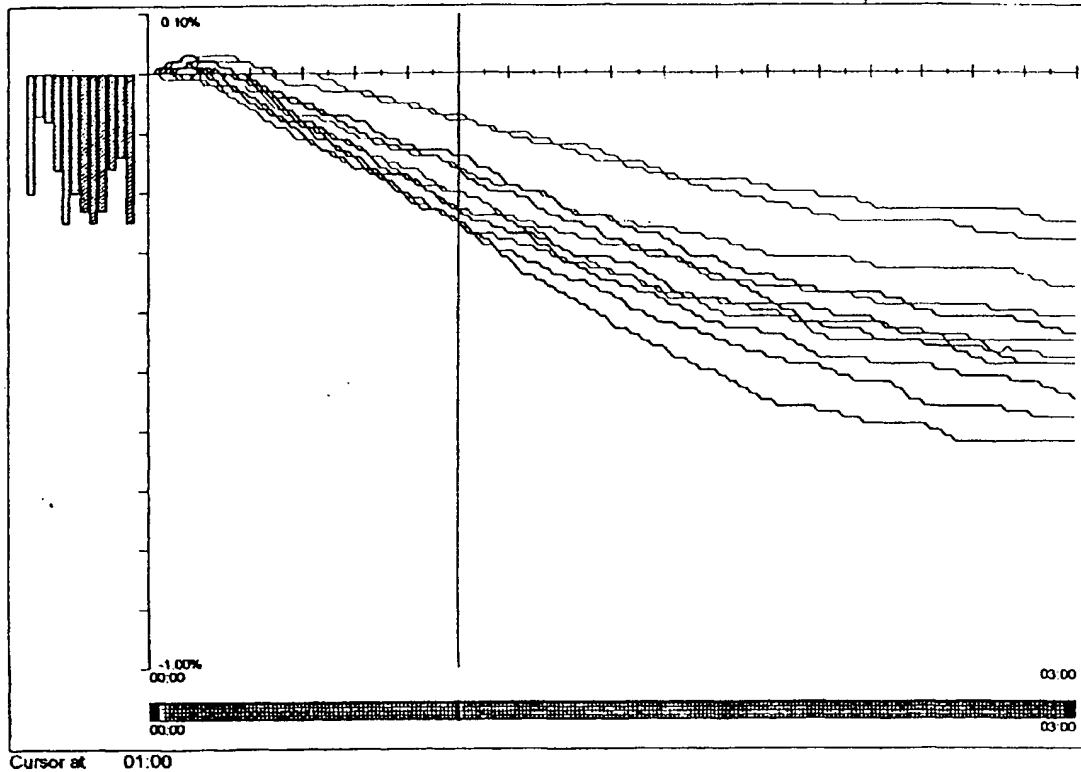


45

wherein R_1 , R_2 , R_3 and R_4 are all different and stand for different organic or inorganic substituents.

6. A sensor as claimed in claim 5, wherein at least one of the substituents R_1 , R_2 , R_3 and R_4 is or contains one or more sulphonate group(s). 50
7. A sensor as claimed in any one of claims any one of claims 2 to 6, wherein the counter-ion is camphor sulphonate, menthoxy acetate, carzyl acetate or natural or synthetic chiral amino acids, e.g. cysteine and valine. 55

8. A sensor as claimed in claim 1, wherein the chiral sites in the polymer material are formed by chiral side groups bonded to the backbone polymer chains, e.g. radicals formed from menthoxy acetic acid, carzyl acetate and natural or synthetic chiral amino acids such as cysteine and valine.
9. A sensor as claimed in claim 1, wherein the chiral sites in the polymer material are formed by growing the polymer from a monomer solution whose solvent is optically active.
10. A method of detecting and discriminating between different chiral compounds, which comprises exposing a sensor as claimed in any one of claims 1 to 9 to a gaseous sample containing an optically active substance and measuring the resistance of the polymer material.



□ -0.20% Type 298	□ -0.07% Type 298	□ -0.08% Type 298	□ -0.16% Type 298
□ -0.25% Type 298	□ -0.20% Type 298	▨ -0.23% Type 297	▨ -0.25% Type 297
▨ -0.23% Type 297	▨ -0.16% Type 297	▨ -0.14% Type 297	▨ -0.25% Type 297

Figure 1

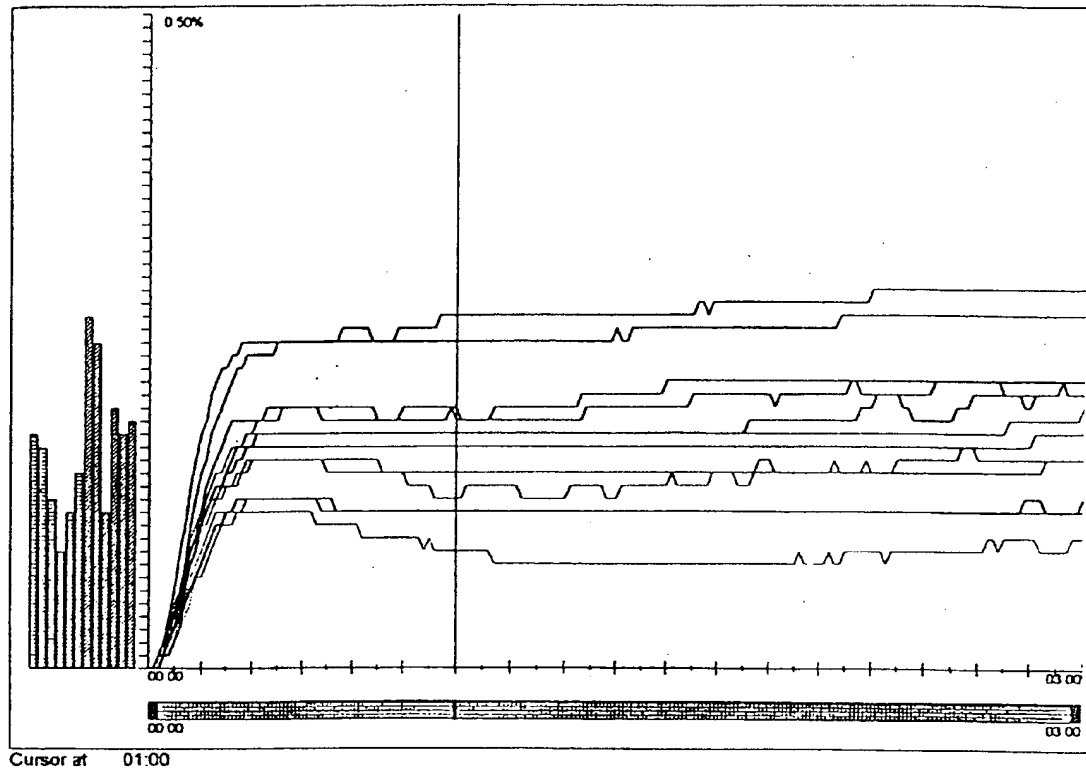
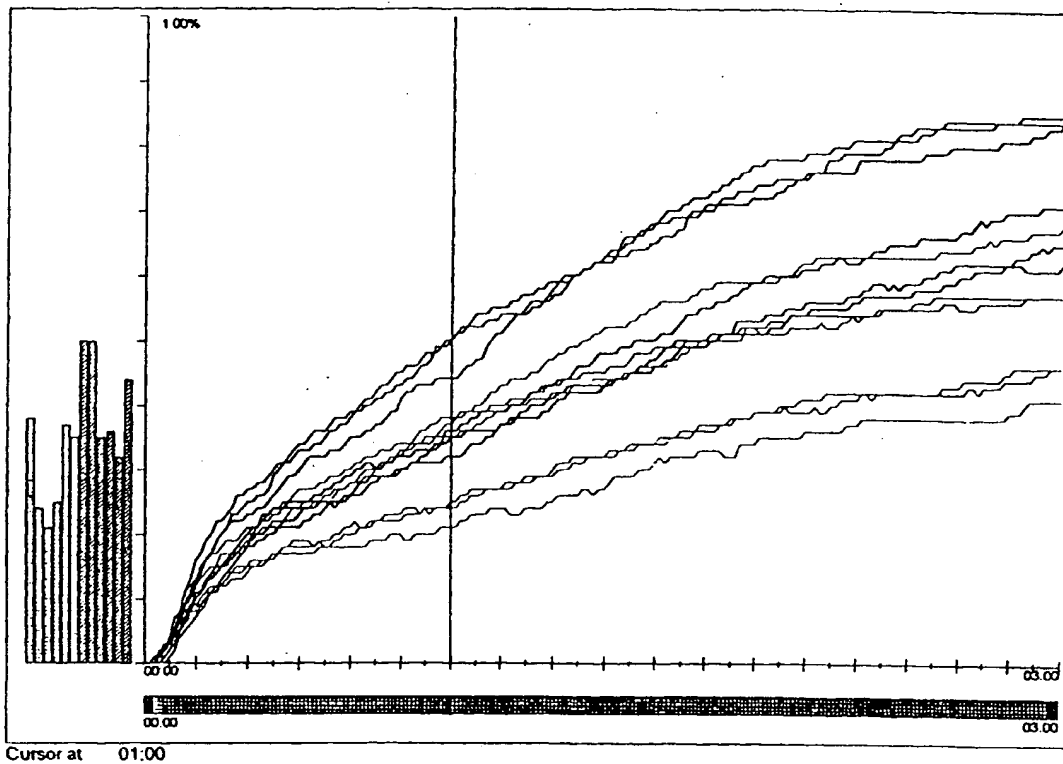


Figure 2



0.38% Type 298	0.24% Type 298	0.21% Type 298	0.25% Type 298
0.37% Type 298	0.35% Type 298	0.50% Type 297	0.50% Type 297
0.35% Type 297	0.36% Type 297	0.32% Type 297	0.44% Type 297

Figure 3

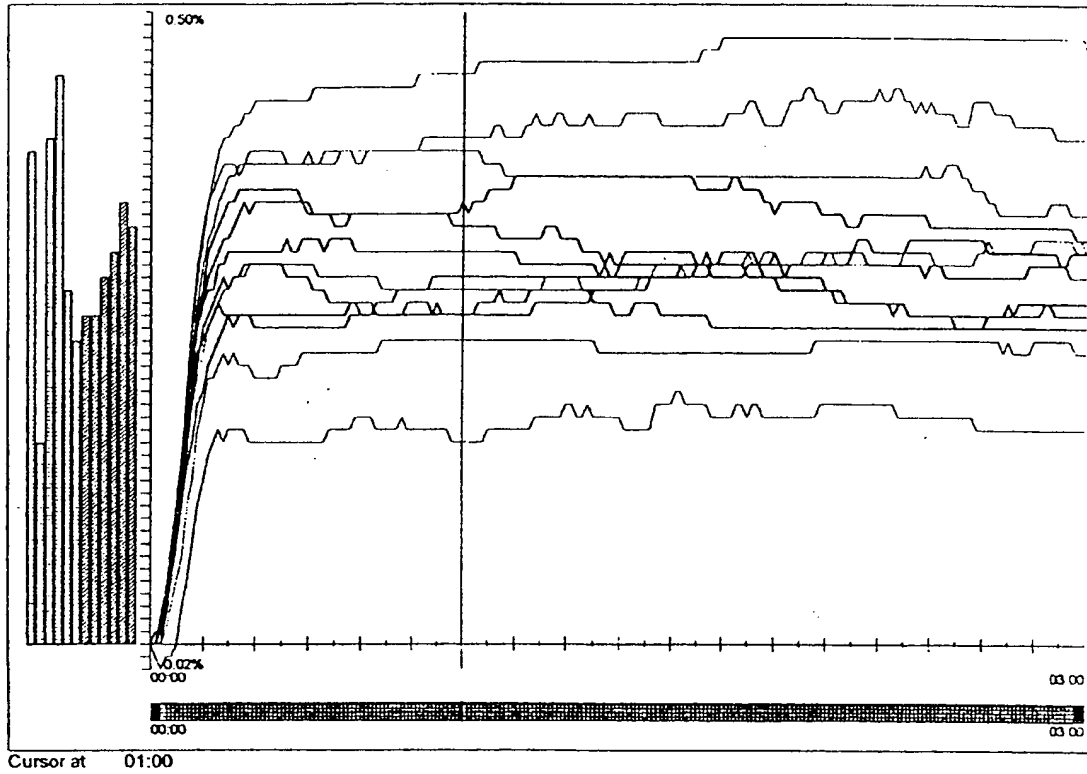
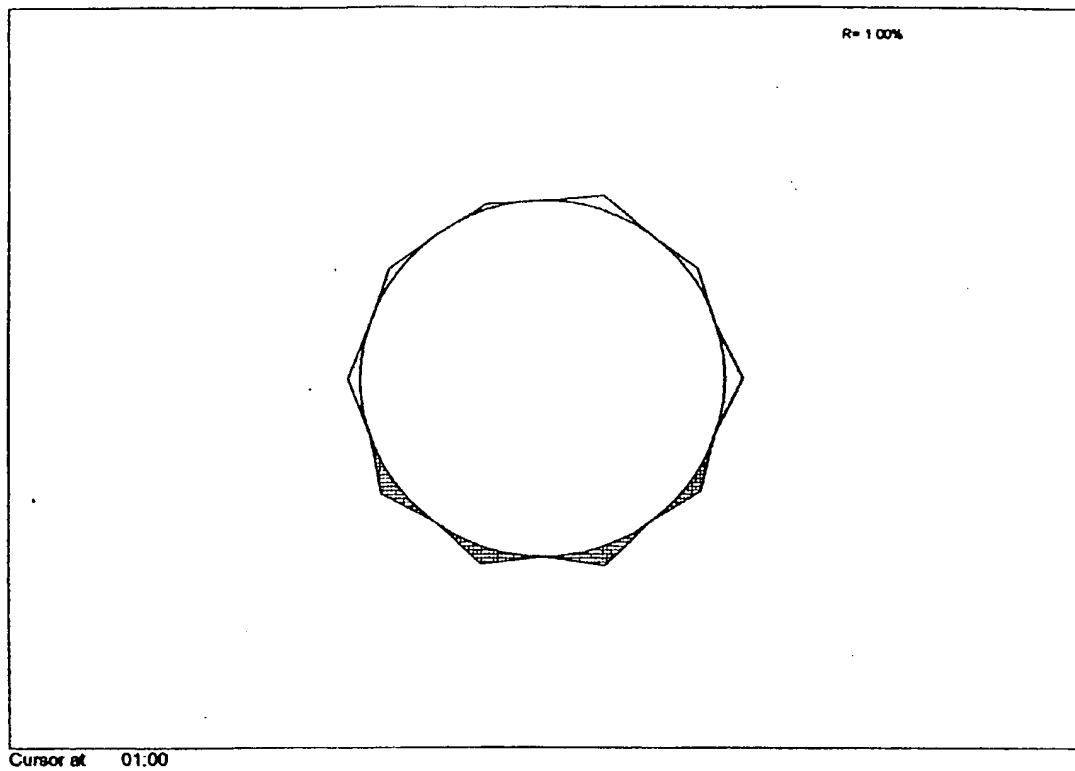
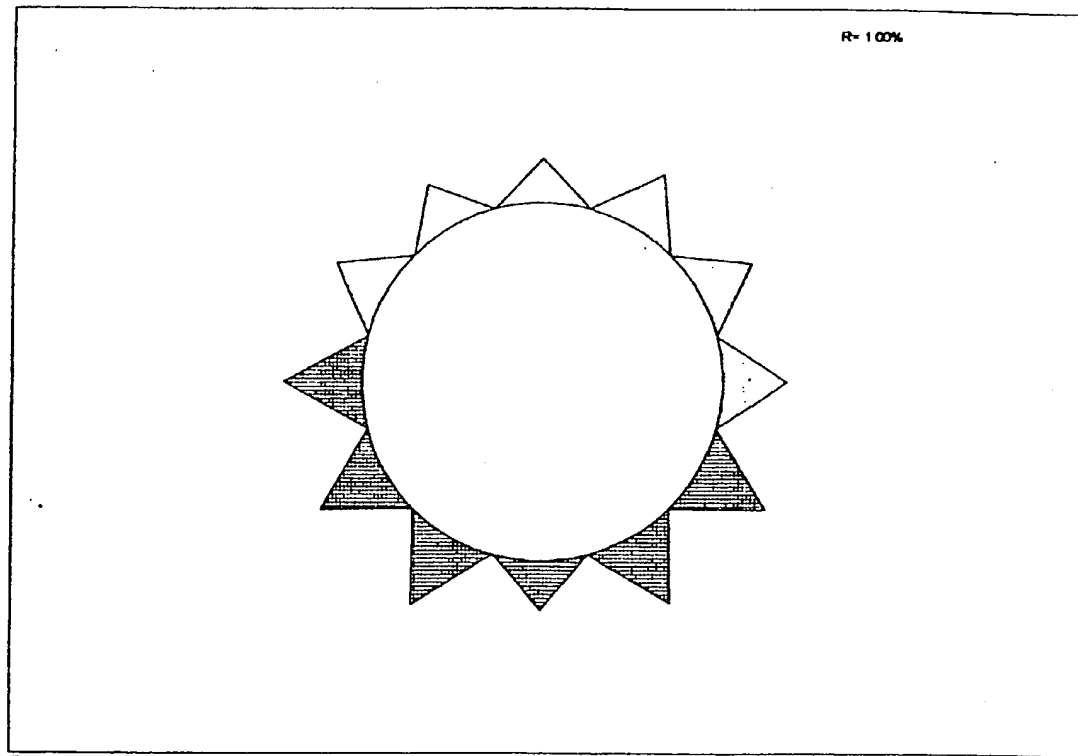


Figure 4



<input checked="" type="checkbox"/> 0.10% Type 531	<input checked="" type="checkbox"/> 0.05% Type 531	<input checked="" type="checkbox"/> 0.08% Type 531	<input checked="" type="checkbox"/> 0.03% Type 531
<input checked="" type="checkbox"/> 0.05% Type 531	<input checked="" type="checkbox"/> 0.07% Type 531	<input checked="" type="checkbox"/> 0.10% Type 530	<input type="checkbox"/> 0.19% Type 530
<input checked="" type="checkbox"/> 0.10% Type 530	<input type="checkbox"/> -0.08% Type 530	<input checked="" type="checkbox"/> 0.11% Type 530	<input checked="" type="checkbox"/> 0.08% Type 530

Figure 5



☒ 0.36% Type 531
☒ 0.27% Type 531
☒ 0.44% Type 530

☒ 0.33% Type 531
☒ 0.33% Type 531
☒ 0.28% Type 530

☒ 0.34% Type 531
☒ 0.48% Type 530
☒ 0.43% Type 530

☒ 0.25% Type 531
☒ 0.43% Type 530
☒ 0.43% Type 530

Figure 6

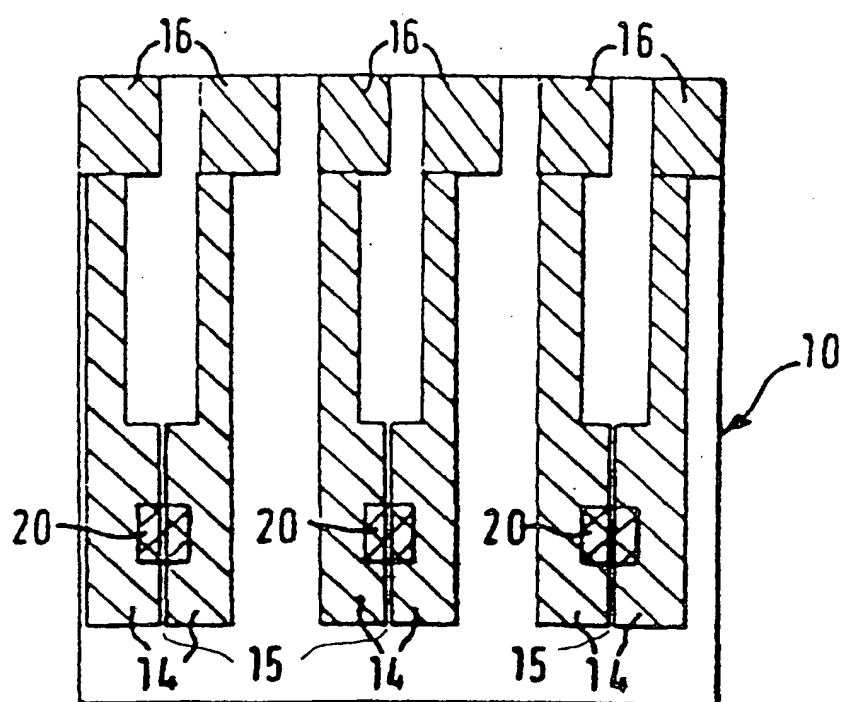


FIG. 7



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 1435

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	HELVETICA CHIMICA ACTA, vol. 70, no. 4, 1987, BASEL CH, pages 942-953, XP000674672 A. KARRER: "STRUCTURES AND ELECTRICAL PROPERTIES OF SOME NEW ORGANIC CONDUCTORS DERIVED FROM THE DONOR MOLECULE TMET" * abstract *	1	G01N27/12
A	GB 2 286 889 A (NEOTRONICS LTD.) * abstract *	1	
D,A	WO 93 03355 A (NEOTRONICS LTD.) * the whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G01N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 June 1997	Examiner Duchatellier, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons * : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.92 (P4/C01)